# Electrochemistry of some Nitrosoaryl Derivatives

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Nitroso aromatics is a class a chemical compounds of biological relevance because of their toxic effects leading to metahemoglobinemia, carcinogenesis, or mutagenesis (1). Such effects are mainly due to a reduction intermediates formation; therefore, the reduction properties of the nitroso group are of prime importance (2). However, the electrochemistry of these type of derivatives has not received great attention, probably due to of difficulties in the synthesis and its chemical instability. On the other hand, most of literature is devoted only to nitrosobenzene (3,4).

In this paper an electrochemical study on the reduction of 2- and 3-nitroso-toluene derivatives and 4--(4-nitroso phenyl)-1,4-dihydro-2, 6-dimethyl-3,5-pyridine dicarboxylic acid diisopropyl ester (Figure 1) is reported in different electrolytic media. Furthermore, UV-Visible and EPR spectroscopic characterization of the corresponding nitroso radical anions in aprotic media is also reported. In protic media (ethanol/0.1 M Britton-Robinson buffer pH 5-12) the derivatives gave a reversible well-defined peak on Hg in the pH range studied in a reaction involving 2electrons to give the hydroxylamine derivative.

In mixed aqueous organic media (0.015 M aqueous citrate/DMF: 60/40 and 0.1 M TBAI) at pH >8 the isolation and the electrochemical characterization of the nitroso radical anion was achieved. Under these experimental conditions, nitroso derivatives were reduced in a quasireversible mechanism.

In aprotic media (0.1 M TBAI in DMF), the nitroso radical anions decayed by a dimerization mechanism, with the following rate constant values: $k_2$= 4,100 $(Ms)^{-1}$, $k_2$ = 2,700 $(Ms)^{-1}$ and $k_2$ = 57,160 $(Ms)^{-1}$ for 2-, 3-nitrosotoluene and the nitroso derivative from 1,4-dihydropyridine derivative, respectively.

References.

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Figure 1. Chemical Structures

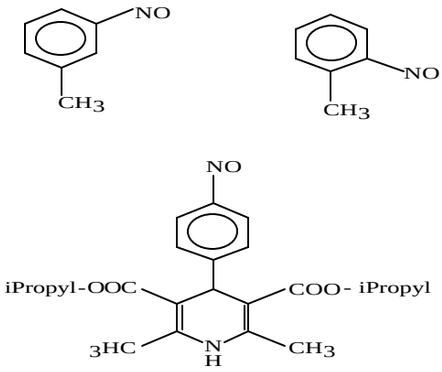


Figure 2. Experimental EPR spectra of:
(1). 0.1 M TBAHPF in acetonitrile (2A) 2-nitrosotoluene (2B) 3-nitrosotoluene (3A-B) Simulated spectra of 2- and 3-nitrosotoluene derivatives

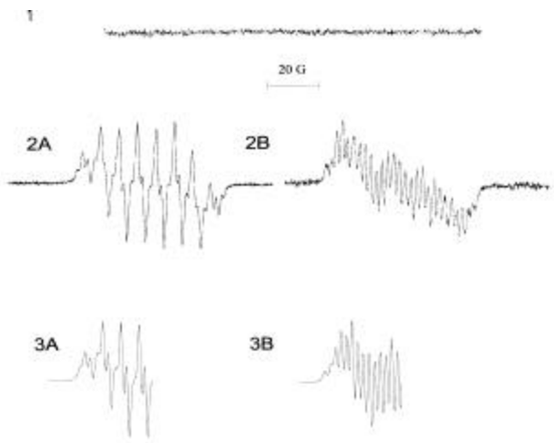


Figure 3. Isolated reversible couples: (A) 2-nitrosotoluene and (B) 3-nitrosotoluene at different sweep rates (1= 0.1, 2= 0.5, 3= 1.0 $Vs^{-1}$) at pH 9 in protic media. Inset: Dependence of $I_{pa}/I_{pc}$ ratio with log v.